Supplementary Information

Electronic structure and spectra of $(Cu_2O)n$-H_2O complexes

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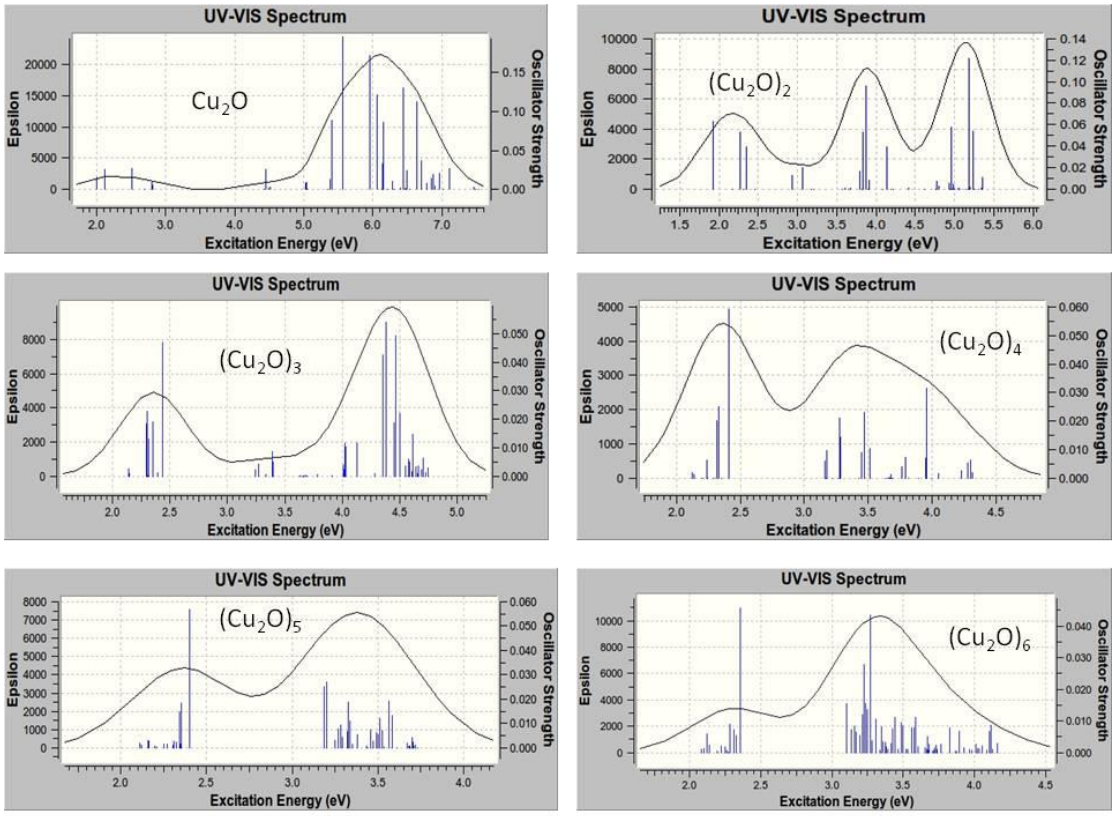

Figure S1: Calculated absorption spectra of $(Cu_2O)_n$ clusters for n=1-6

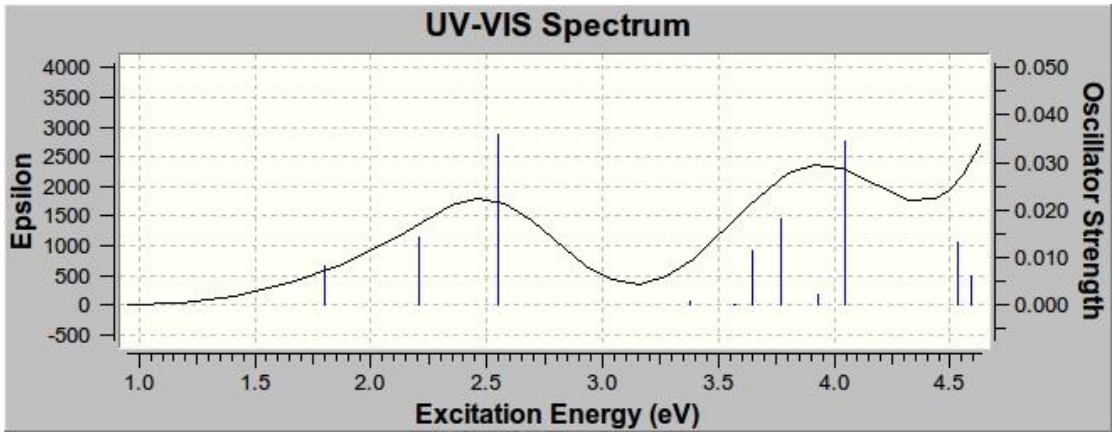

Figure S2: Calculated absorption spectrum of Cu_2O-OH_2 at the optimum geometry of the first excited singlet state.

Coordinates x,y,z for the optimum structures

Cu2O_6311gdp_b3lyp

O	0.00000000	0.00000000	0.89949500
Cu	0.00000000	1.42780000	-0.12406800
Cu	0.00000000	-1.42780000	-0.12406800

Cu4O2_b3lyp_6311gdp

O	-1.50196200	0.00000400	0.42105700
O	1.50175600	-0.00000300	-0.42034700
Cu	3.19955700	-0.00000200	0.05402900
Cu	-0.00010000	-1.10148100	0.00035200
Cu	-0.00008800	1.10148100	0.00035100
Cu	-3.19931200	0.00000200	-0.05492800

Cu6O3_b3lyp_6311gdp

O	-2.01267800	-0.00316800	-0.59562600
O	0.91512000	1.80528400	0.48969600
O	0.91957200	-1.80374600	0.49129300
Cu	1.90574300	3.04506200	-0.27747900
Cu	1.30018900	0.00135400	0.56173300
Cu	-0.72152000	1.22271000	-0.11330200

Cu	-3.62972000	-0.00336300	0.11325000
Cu	1.91283100	-3.04003200	-0.27809800
Cu	-0.71842300	-1.22528100	-0.11241000

Cu8O4_6311gdp_b3lyp

O	-1.70674000	1.81258300	0.56586400
Cu	-2.91861300	2.80427300	-0.25653900
Cu	-1.87571800	0.00540900	0.55293500
O	1.70972800	-1.81606500	-0.55696800
Cu	-0.00697500	-1.94638800	-0.00274200
Cu	2.91700300	-2.80042300	0.28104000
O	1.71872000	1.79958400	-0.56338000
Cu	0.00716000	1.94324800	0.00324600
Cu	1.87565600	-0.00857200	-0.55285000
O	-1.72170900	-1.80301800	0.55433700
Cu	-2.93916400	-2.77894800	-0.27870000
Cu	2.94065200	2.78330900	0.25365200

Cu10O5_6311gdp_b3lyp

O	1.81217600	2.45020300	-0.27707400
O	2.84706600	-1.00058400	-0.30548500
O	-0.08584200	-3.06693800	-0.05604800
O	-2.91734800	-0.88354400	0.35916400
O	-1.78187500	2.49789600	-0.12404300
Cu	2.40511600	0.74687000	-0.24054000

Cu	1.41310100	-2.07855000	-0.18222100
Cu	-1.53108200	-2.01455500	0.15873700
Cu	-2.39790500	0.82416400	0.12392600
Cu	0.01586400	2.52427100	-0.20632700
Cu	4.25095600	-1.52040200	0.63896700
Cu	2.59058400	3.58948300	0.83450300
Cu	-2.56258400	3.33498300	-1.48003700
Cu	-3.86151300	-1.16194700	1.83353200
Cu	-0.28782800	-4.24349900	-1.36923400

Cu12O6_6311gdp_b3lyp

O	-3.02531500	1.89289600	0.18877700
O	0.13913300	3.54236300	-0.21215000
O	3.17480900	1.66996700	0.20780700
O	3.03953500	-1.89845900	-0.20790200
O	-0.12744600	-3.55261500	0.18017800
O	-3.16828600	-1.67766200	-0.18370200
Cu	1.65954200	2.61050900	-0.00198700
Cu	3.10691200	-0.11501900	0.00259600
Cu	1.45556600	-2.72621900	-0.02111900
Cu	-1.64932200	-2.61699800	-0.00932700
Cu	-3.10758100	0.10890000	-0.00065000
Cu	-1.44573000	2.72186600	-0.01624700
Cu	4.04602300	2.16433200	1.66839200
Cu	0.16574000	4.55227100	-1.67192700
Cu	-3.88610900	2.45029900	1.63867700

Cu	-4.11401700	-2.15026300	-1.60356400
Cu	-0.16720600	-4.53316700	1.66131400
Cu	3.92723600	-2.46002600	-1.63871200

Ring structures with water

Cu2O_H2O_6311gdp_b3lyp

O	-1.07334700	-0.37718100	0.00000000
Cu	0.00000000	1.02362300	0.00000000
Cu	-0.10698300	-1.83822300	0.00000000
O	1.10465900	2.57398800	0.00000000
H	0.78756300	3.48094400	0.00000000
H	2.06443700	2.56800300	0.00000000

Cu4O2_H2O_6311gdp_b3lyp

O	-1.18752000	0.00529300	-0.79622300
O	1.77597400	-0.00107100	0.20933800
Cu	3.52772300	-0.00415900	0.41581400
Cu	0.29888500	1.09961500	-0.31599000
Cu	0.29835600	-1.09335900	-0.32770900
Cu	-2.72726400	0.00045400	0.06821200
O	-4.41079600	-0.00213300	0.94866600

H	-4.93114500	-0.81300400	0.95574600
H	-5.02342300	0.72229000	0.78049400

Cu6O3_H2O_6311gdp_b3lyp

O	-1.71677600	-0.01206000	-0.76068500
O	1.12995700	1.81235200	0.51462300
O	1.15396400	-1.79906100	0.51350700
Cu	2.16036300	3.04271000	-0.21325300
Cu	1.51596100	0.00886500	0.62090900
Cu	-0.45378900	1.21298100	-0.21242900
Cu	-3.34416100	-0.01845500	-0.06601700
Cu	2.19944400	-3.02163100	-0.20574700
Cu	-0.43820600	-1.22237600	-0.21389200
O	-5.09897600	-0.03246100	0.64952300
H	-5.75703200	-0.61735500	0.25878100
H	-5.53703200	0.80645200	0.82791600

Cu8O4_H2O_6311gdp_b3lyp

O	0.48810700	-2.46623600	0.55677300
Cu	0.93413400	-3.89870700	-0.38345300
Cu	1.68185200	-1.09778200	0.61737300
O	-0.03489800	2.49659300	-0.65277800
Cu	1.37705200	1.57999400	0.01119200
Cu	-0.50395700	3.97587700	0.19874400
O	-2.21526300	-0.39167900	-0.63944700

Cu	-0.93632600	-1.53232300	-0.06207200
Cu	-1.24429000	1.13887400	-0.65996300
O	2.62932600	0.45142000	0.67022700
Cu	4.22397800	0.49220300	-0.09582100
Cu	-3.82277300	-0.46656200	0.09596600
O	-5.55921100	-0.56069000	0.84950800
H	-6.31782300	-0.57291100	0.25556200
H	-5.72710400	-1.21797700	1.53323200

Cu10O5_H2O_6311gdp_b3lyp

O	2.63584300	1.80786000	-0.14883300
O	2.63491100	-1.79550600	-0.15959600
O	-0.78562400	-2.90297800	-0.25888100
O	-2.88795800	-0.00047600	0.08740600
O	-0.78834100	2.90165800	-0.27577700
Cu	2.70799700	0.00597800	-0.09428100
Cu	0.94026000	-2.39774900	-0.20805500
Cu	-1.87073600	-1.47275300	-0.09640400
Cu	-1.87304500	1.47240900	-0.10469800
Cu	0.93858500	2.40228300	-0.21332300
Cu	3.67298000	-2.67115000	0.97661700
Cu	3.63537600	2.67605000	1.02744000
Cu	-1.20846800	3.82392000	-1.73370200
Cu	-4.07325000	-0.00655500	1.40373800
Cu	-1.20326400	-3.82452000	-1.71847700
O	-5.36992000	-0.01034100	2.78760800

H	-6.09629100	0.62074600	2.74553800
H	-5.74157100	-0.85195900	3.07224900

Cu12O6_H2O_6311gdp_b3lyp

O	3.42474900	-0.04649900	-0.03640500
O	1.57680800	-3.11131000	-0.37374200
O	-1.95999200	-3.07574600	0.26159000
O	-3.74050900	0.03682300	0.01416500
O	-1.90163200	3.11860500	0.21801000
O	1.64905900	3.06552800	-0.32712500
Cu	-0.18972400	-3.09780500	-0.04839900
Cu	-2.85359900	-1.52147600	0.14261300
Cu	-2.82366500	1.57964400	0.11923600
Cu	-0.12467600	3.09744300	-0.05238700
Cu	2.53498500	1.50540500	-0.20114000
Cu	2.49691300	-1.57270200	-0.22395300
Cu	-2.41196400	-3.99261900	1.71095400
Cu	1.92580500	-3.84526100	-1.95428700
Cu	4.65300400	-0.07722000	1.24077700
Cu	2.11623200	3.89078700	-1.82833600
Cu	-2.34568700	4.05715700	1.65671300
Cu	-4.80288800	0.03821500	-1.40872700
O	5.98937100	-0.09978600	2.58653600
H	6.86656100	-0.43019900	2.36486500
H	5.76322900	-0.45619000	3.45204900

Barel structures

geom_start_3-Cu12O6

O	-3.35917100	0.00000000	0.00000000
O	-1.67958500	2.90912700	0.00000000
O	1.67958500	2.90912700	0.00000000
O	3.35917100	0.00000000	0.00000000
O	1.67958500	-2.90912700	0.00000000
O	-1.67958500	-2.90912700	0.00000000
Cu	0.00000000	4.21655900	0.00000000
Cu	0.00000000	1.87987800	0.00000000
Cu	3.06507600	1.76962300	1.18610200
Cu	3.06507600	1.76962300	-1.18610200
Cu	3.65164700	-2.10827900	0.00000000
Cu	1.62802200	-0.93993900	0.00000000
Cu	0.00000000	-3.53924500	1.18610200
Cu	0.00000000	-3.53924500	-1.18610200
Cu	-3.65164700	-2.10827900	0.00000000
Cu	-1.62802200	-0.93993900	0.00000000
Cu	-3.06507600	1.76962300	1.18610200
Cu	-3.06507600	1.76962300	-1.18610200
O	-2.90912700	1.67958500	-3.56013100
O	0.00000000	3.35917100	-3.56013100
O	2.90912700	1.67958500	-3.56013100

O	2.90912700	-1.67958500	-3.56013100
O	0.00000000	-3.35917100	-3.56013100
O	-2.90912700	-1.67958500	-3.56013100
Cu	1.76962300	3.06507600	-2.37403000
Cu	1.76962300	3.06507600	-4.74623300
Cu	4.21655900	0.00000000	-3.56013100
Cu	1.87987800	0.00000000	-3.56013100
Cu	1.76962300	-3.06507600	-2.37403000
Cu	1.76962300	-3.06507600	-4.74623300
Cu	-2.10827900	-3.65164700	-3.56013100
Cu	-0.93993900	-1.62802200	-3.56013100
Cu	-3.53924500	0.00000000	-2.37403000
Cu	-3.53924500	0.00000000	-4.74623300
Cu	-2.10827900	3.65164700	-3.56013100
Cu	-0.93993900	1.62802200	-3.56013100
O	-2.90912700	1.67958500	3.56013100
O	0.00000000	3.35917100	3.56013100
O	2.90912700	1.67958500	3.56013100
O	2.90912700	-1.67958500	3.56013100
O	0.00000000	-3.35917100	3.56013100
O	-2.90912700	-1.67958500	3.56013100
Cu	1.76962300	3.06507600	4.74623300
Cu	1.76962300	3.06507600	2.37403000
Cu	4.21655900	0.00000000	3.56013100
Cu	1.87987800	0.00000000	3.56013100
Cu	1.76962300	-3.06507600	4.74623300
Cu	1.76962300	-3.06507600	2.37403000

Cu	-2.10827900	-3.65164700	3.56013100
Cu	-0.93993900	-1.62802200	3.56013100
Cu	-3.53924500	0.00000000	4.74623300
Cu	-3.53924500	0.00000000	2.37403000
Cu	-2.10827900	3.65164700	3.56013100
Cu	-0.93993900	1.62802200	3.56013100

geom_partially-opt_3-Cu12O6_m062x_lanl2dz

O	-0.00957900	1.86909900	1.35115000
O	-0.12979300	-0.82700800	3.84013000
O	-0.09095500	-2.08581100	0.91706500
O	0.06398000	-2.91588000	-2.66198300
O	0.09612000	0.25501600	-2.29132200
O	0.07141600	3.75078100	-1.21888900
Cu	-0.13305100	-2.59688300	2.96925900
Cu	-0.06334100	-0.11420500	1.78081800
Cu	-1.82983900	-3.08763000	-2.63877600
Cu	1.95253400	-3.09182400	-2.54712300
Cu	0.11420600	-1.27032900	-3.74840900
Cu	-0.00091900	-1.47625600	-1.01363100
Cu	-1.81866000	3.79519200	-1.42090500
Cu	1.96834100	3.77353000	-1.35512600
Cu	0.02977400	3.89519000	0.74968600
Cu	0.05519500	1.60910200	-0.78173600
Cu	-2.02383200	-0.67777300	3.91281000
Cu	1.76193900	-0.71061200	3.99926600

O	3.65834200	-0.77446400	3.67889100
O	3.58616100	-2.98393900	1.33799200
O	3.84167500	-2.77546900	-2.34221100
O	3.82215600	0.35632500	-3.08189200
O	3.85065000	3.45910300	-1.09487200
O	3.69214100	2.49649200	1.97550200
Cu	1.70858100	-2.73223500	0.99712700
Cu	4.03936100	-3.23838700	-0.49855400
Cu	4.18369400	-1.48757000	-3.84087400
Cu	3.90651200	-0.85713800	-1.44131300
Cu	1.92519500	0.50734300	-2.78196600
Cu	4.19273700	2.10649400	-2.40341700
Cu	4.13208900	4.07687400	0.78774200
Cu	3.79595200	1.69578300	0.09613300
Cu	1.79513600	2.17684500	1.89414400
Cu	4.01249800	1.02974200	3.15814600
Cu	3.94758900	-2.72326400	3.31412800
Cu	3.71638100	-0.95131900	1.56028700
O	-3.90807900	-0.69500600	3.51347300
O	-3.81040600	-2.89088300	1.16406400
O	-3.71883800	-2.74597800	-2.51116700
O	-3.59097300	0.39395500	-3.20473200
O	-3.71482300	3.51134700	-1.23115500
O	-3.70894200	2.60754400	1.85904300
Cu	-4.12386700	-3.20871100	-0.69945800
Cu	-1.91525200	-2.65030500	0.91538300
Cu	-4.04466300	-1.42102400	-3.97372800

Cu	-3.63813600	-0.84167400	-1.56670100
Cu	-3.98549400	2.13705400	-2.53265500
Cu	-1.70093500	0.54371300	-2.87564900
Cu	-4.06384900	4.17554000	0.62489700
Cu	-3.78084700	1.77148300	-0.01003600
Cu	-4.13222300	1.12855300	2.98978900
Cu	-1.82039000	2.23349300	1.83894500
Cu	-4.18492000	-2.64709400	3.14349400
Cu	-3.97756600	-0.87314000	1.39825400

2-ring_geom_2-Cu12O6_b3lyp_lanl2dz

O	-0.56405600	-3.70687800	-1.85344600
O	-3.47189500	-1.35909300	-1.93063600
O	-2.94688100	2.34234100	-1.86232500
O	0.54807600	3.66735600	-1.94492800
O	3.49673900	1.37013700	-1.87443400
O	2.90589600	-2.32036700	-1.93352300
Cu	-3.18294200	0.51404600	-2.04363000
Cu	-1.21518000	2.97275800	-2.05071100
Cu	2.03060400	2.48710900	-2.06144700
Cu	3.18496100	-0.44700600	-2.05594500
Cu	1.13814800	-3.00226300	-2.04259400
Cu	-1.98428600	-2.53315200	-2.04433400
Cu	-3.04568700	2.42827900	0.01486700
Cu	-4.79478800	-1.83987800	-3.12366500

Cu	-0.58248500	-3.82823000	0.02228100
Cu	4.00266900	-3.21970800	-3.11330400
Cu	3.61943900	1.41868700	0.00073100
Cu	0.73451500	5.12421800	-3.05958100
O	-0.55191000	-3.66921200	1.94076600
O	-3.49688600	-1.36748100	1.86316000
O	-2.90790200	2.32339700	1.93091200
O	0.56370600	3.70330000	1.84929900
O	3.47399400	1.35867400	1.91820900
O	2.94101400	-2.34057600	1.85948700
Cu	-3.18190700	0.44849800	2.04556100
Cu	-1.13754600	2.99641600	2.04053000
Cu	1.98463700	2.53020500	2.03649600
Cu	3.18246500	-0.51290100	2.04039300
Cu	1.21108200	-2.97462400	2.04776300
Cu	-2.03189500	-2.48530800	2.05289300
Cu	-3.97287200	3.15518300	3.18862600
Cu	-3.61790300	-1.41770600	-0.01272300
Cu	-0.76050000	-5.10160100	3.08405700
Cu	3.04217600	-2.42284700	-0.01674800
Cu	4.80072500	1.88330800	3.08708900
Cu	0.57935700	3.82607700	-0.02627200

3-ring_geom_3-Cu8O4_b3lyp_lanl2dz

O	-3.74784600	0.83446700	-2.50549000
Cu	-3.86991400	1.80195000	-0.90915300

O	-3.74620600	-0.83286400	2.51185900
Cu	-3.87344300	0.89493100	1.80556200
Cu	-1.88335000	-0.91351200	2.75899000
O	-3.78082900	-2.56476400	-0.85080000
Cu	-3.87377300	-0.89311700	-1.79873800
Cu	-3.86850900	-1.79846700	0.91358400
O	-3.77721800	2.56529800	0.85603500
Cu	-1.89326800	-2.81749800	-0.93392900
O	0.01825500	0.85207800	-2.58019800
Cu	-1.88576900	0.91220000	-2.75981100
Cu	-0.00137000	1.81018000	-0.91123500
O	0.01977900	-0.85684900	2.57295200
Cu	-0.00031900	0.91128200	1.81616000
Cu	1.88972100	-0.93387100	2.81547500
O	-0.02265100	-2.57773100	-0.86110500
Cu	-0.00047800	-0.91398500	-1.81848700
Cu	-0.00162200	-1.81481500	0.90710600
O	-0.02021900	2.57484500	0.85868400
Cu	-1.88973500	2.81912200	0.93502200
Cu	1.88151400	-2.76070600	-0.91377500
O	3.77564600	0.85065900	-2.56761300
Cu	1.88841200	0.92941900	-2.82323100
Cu	3.87699900	1.79747000	-0.89822300
O	3.77772600	-0.85505900	2.56390000
Cu	3.86556200	0.91063800	1.79652100
O	3.74418300	-2.51414100	-0.83046200
Cu	3.86355800	-0.91543800	-1.79936100

Cu	3.87500300	-1.80495500	0.89483500
O	3.74681100	2.50719000	0.82421200
Cu	1.88401500	2.75583400	0.90867400
Cu	-5.08351400	3.80644300	1.21889800
Cu	-5.09326300	-3.79501200	-1.22286100
Cu	5.10452900	1.23711900	-3.77385000
Cu	5.09248300	-1.22055800	3.79404000

CI calculations

Cu36O18_barel_H2O for CI calculations

O	0.000000000000	3.359170936338	0.000000000000
O	2.909127366193	1.679585468741	0.000000000000
O	2.909127367183	-1.679585467025	0.000000000000
O	0.000000001981	-3.359170936338	0.000000000000
O	-2.909127365202	-1.679585470457	0.000000000000
O	-2.909127368174	1.679585465309	0.000000000000
Cu	4.216558832014	0.000000001243	0.000000000000
Cu	1.879877951257	0.000000000554	0.000000000000
Cu	1.769622655567	-3.065076346187	1.186101621212
Cu	1.769622655567	-3.065076346187	-1.186101621212
Cu	-2.108279413494	-3.651647066527	0.000000000000
Cu	-0.939938974508	-1.628022062450	0.000000000000
Cu	-3.539245308120	-0.000000003131	1.186101621212

Cu -3.539245308120 -0.000000003131 -1.186101621212

Cu -2.108279419956 3.651647062796 0.000000000000

Cu -0.939938977389 1.628022060787 0.000000000000

Cu 1.769622650143 3.065076349318 1.186101621212

Cu 1.769622650143 3.065076349318 -1.186101621212

O 1.679585466428 2.909127367528 -3.560131200841

O 3.359170936338 0.000000002670 -3.560131200841

O 1.679585471053 -2.909127364858 -3.560131200841

O -1.679585464713 -2.909127368518 -3.560131200841

O -3.359170936338 -0.000000004651 -3.560131200841

O -1.679585472769 2.909127363867 -3.560131200841

Cu 3.065076348638 -1.769622651322 -2.374029579629

Cu 3.065076348638 -1.769622651322 -4.746232822054

Cu 0.000000004595 -4.216558832014 -3.560131200841

Cu 0.000000002049 -1.879877951257 -3.560131200841

Cu -3.065076344781 -1.769622658003 -2.374029579629

Cu -3.065076344781 -1.769622658003 -4.746232822054

Cu -3.651647068203 2.108279410592 -3.560131200841

Cu -1.628022063197 0.939938973214 -3.560131200841

Cu -0.000000005944 3.539245308120 -2.374029579629

Cu -0.000000005944 3.539245308120 -4.746232822054

Cu 3.651647061120 2.108279422858 -3.560131200841

Cu 1.628022060040 0.939938978683 -3.560131200841

O 1.679585466428 2.909127367528 3.560131200841

O 3.359170936338 0.000000002670 3.560131200841

O 1.679585471053 -2.909127364858 3.560131200841

O -1.679585464713 -2.909127368518 3.560131200841

O -3.359170936338 -0.000000004651 3.560131200841

O -1.679585472769 2.909127363867 3.560131200841

Cu 3.065076348638 -1.769622651322 4.746232822054

Cu 3.065076348638 -1.769622651322 2.374029579629

Cu 0.000000004595 -4.216558832014 3.560131200841

Cu 0.000000002049 -1.879877951257 3.560131200841

Cu -3.065076344781 -1.769622658003 4.746232822054

Cu -3.065076344781 -1.769622658003 2.374029579629

Cu -3.651647068203 2.108279410592 3.560131200841

Cu -1.628022063197 0.939938973214 3.560131200841

Cu -0.000000005944 3.539245308120 4.746232822054

Cu -0.000000005944 3.539245308120 2.374029579629

Cu 3.651647061120 2.108279422858 3.560131200841

Cu 1.628022060040 0.939938978683 3.560131200841

O 2.298799904567 -5.181785342187 1.186101621212

H 3.055523370637 -5.767584556830 1.186101621212

H 1.542076438497 -5.767584556830 1.186101621212

Cu24O12_barel_H2O for CI calculations

O 0.000000000000 3.337887475092 0.000000000000

O 2.890695348075 1.668943738114 0.000000000000

O 2.890695349059 -1.668943736409 0.000000000000

O 0.000000001969 -3.337887475092 0.000000000000

O -2.890695347091 -1.668943739819 0.000000000000

O -2.890695350044 1.668943734704 0.000000000000

Cu 4.172737944569 0.000000001231 0.000000000000

Cu 1.881469482610 0.000000000555 0.000000000000

Cu 1.741842465795 -3.016959646114 1.173150817989

Cu 1.741842465795 -3.016959646114 -1.173150817989

Cu -2.086368969798 -3.613697064767 0.000000000000

Cu -0.940734740184 -1.629400369033 0.000000000000

Cu -3.483684928625 -0.000000003082 1.173150817989

Cu -3.483684928625 -0.000000003082 -1.173150817989

Cu -2.086368976192 3.613697061076 0.000000000000

Cu -0.940734743067 1.629400367368 0.000000000000

Cu 1.741842460457 3.016959649196 1.173150817989

Cu 1.741842460457 3.016959649196 -1.173150817989

O 1.668943735816 2.890695349402 -3.538765072605

O 3.337887475092 0.000000002653 -3.538765072605

O 1.668943740412 -2.890695346748 -3.538765072605

O -1.668943734111 -2.890695350386 -3.538765072605

O -3.337887475092 -0.000000004622 -3.538765072605

O -1.668943742117 2.890695345764 -3.538765072605

Cu 3.016959648526 -1.741842461618 -2.365614254617

Cu 3.016959648526 -1.741842461618 -4.711915890594

Cu 0.000000004547 -4.172737944569 -3.538765072605

Cu 0.000000002050 -1.881469482610 -3.538765072605

Cu -3.016959644729 -1.741842468193 -2.365614254617

Cu -3.016959644729 -1.741842468193 -4.711915890594

Cu -3.613697066426 2.086368966925 -3.538765072605

Cu -1.629400369781 0.940734738889 -3.538765072605

Cu -0.000000005851 3.483684928625 -2.365614254617

Cu -0.000000005851 3.483684928625 -4.711915890594

Cu 3.613697059417 2.086368979064 -3.538765072605

Cu 1.629400366621 0.940734744362 -3.538765072605

O 2.298799904567 -5.181785342187 -1.186101621212

H 3.055523370637 -5.767584556830 -1.186101621212

H 1.542076438497 -5.767584556830 -1.186101621212

Cu8O4_H2O for CI calculations

O 0.000000000000 0.000000000000 0.000000000000

O 1.957163855370 -3.201938028566 -3.504433633354

O -1.182796777844 -2.944528365451 -1.724111784984

O 3.088158220329 -0.182623218438 -1.881278157937

Cu 0.000000000000 0.000000000000 1.770499540632

Cu 1.611797583728 0.000000000000 -0.838564577445

Cu 2.637028625800 -1.699395087652 -2.759799677477

Cu 1.978297996744 -3.302590961187 -5.271504701373

Cu -0.694103928256 -1.478076682800 -0.785747208259

Cu 0.323574588483 -3.169412496943 -2.706858893573

Cu 4.678380311660 -0.151458098333 -1.105803478033

Cu -2.791511054133 -2.992272372754 -2.458970871060

O -4.525166368819 -3.071728266681 -3.220364156380

H -5.049862680449 -3.868611396194 -3.086182905272

H -5.116041995205 -2.321726361661 -3.093967380581

Details of the Configuration Interaction Method and calculations

Theory

Electronic systems are described by a configuration interaction embedding method that is designed to give an accurate many-electron description of the adsorbate-surface region of a metal or oxide and electron transfer states. Many applications of the method to ground and excited states of adsorbates on metals have been reported previously and details of the method can be found in earlier publications and previous progress reports. A brief summary is given below.

Calculations are carried out for the full electrostatic Hamiltonian of the system (except for core electron potentials)

$$\mathrm{H} = \sum_{\mathrm{i}}^{\mathrm{N}} [-\tfrac{1}{2}\nabla_i^2 + \sum_{k}^{Q}(\frac{-Z_k}{r_{ik}} + V_{ik}^{core})] + \sum_{i<j}^{N} \frac{1}{r_{ij}}$$

Wavefunctions are constructed by self-consistent-field (SCF) and multi-reference configuration interaction (CI) expansions

$$\Psi = \sum_k c_k (n!)^{-1/2} det\,(\chi_1^k\ \chi_2^k \ldots \chi_n^k) = \sum_k c_k \Phi_k$$

In the present work, the electron transfer state to the adsorbed water molecule lies several eV above the ground state and even for the small clusters investigated many intervening lower energy states exist.

In order to focus on the electron transfer excited states relevant to the dissociation of water we proceed as follows. An initial, single-determinant, self-consistent field (SCF) calculatios on the positive ion of the water-cluster complex are carried out. Examination of the virtual eigenvalue spectrum allows the positive ion orbitals containing appreciable contributions from water basis functions to be identified. CI calculations on the neutral water-cluster complex are performed using the positive ion occupied and virtual orbitals. Configurations involving water and the ground state configuration are used as initial descriptions of the states and single and double excitations from each ground and excited configuration are generated. Proceeding in this way allows one to construct electronic states that are orthogonal to and effectively non-interacting with lower lying states and thereby assuring an upper bound on the excited state energy. Not all occupied orbitals are included in the active space of the configuration interaction and this means that there is an energy defect

associated with the description of the ground state using positive ion orbitals. This defect is calculated by performing a constrained SCF calculation on the ground state using a fixed core of positive ion orbitals and comparing the result with the unconstrained SCF calculation. The energy defects calculated in this way are ~0.25eV but vary slightly for the different clusters calculated.

Cu8O4

active electrons in CI= 22

Threshold for single and double excitation

(selection based on second order perturbation energy)= 3x10-6

determinants in CI 72033

Ground state defect=0.30eV

Cu24O12

active electrons in CI= 18

Threshold for single and double excitation

(selection based on second order perturbation energy)= 2x10-6

determinants in CI 54246

Ground state defect=0.26eV

Cu36O18 tube

active electrons in CI= 18

Threshold for single and double excitation

(selection based on second order perturbation energy)= 2x10-6

determinants in CI 59909

Ground state defect=0.26eV

Copper. Basis simplex optimization of exponents and coefficients for Cu ^{1}S ground state

Orbital (number of gaussians in expansion)

1s (12)

2s (10)

3s (7)

4s (4)

2p (7)

3p (6)

4p (2)

Oxygen. (Hartree-Fock atomic orbitals plus additional correlation basis functions plus a diffuse Rydberg-like oxygen basis function.

1s (8)

2s (5)

2s’ (1)

2p (5)

2p’ (1)

s’ (3)

p’ (3)

d’ (2)

s’’ (1) 0.05 exp

Hydrogen

1s (5)

1s’ (1)

2p (1)